Nonequilibrium thermodynamics of colloids

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Abstract

The common rules of classical nonequilibrium thermodynamics do not allow
an Onsager coefficient like the viscosity to depend on the shear rate. Such a
dependence is experimentally well documented, however. In this paper it is
shown, using nonequilibrium thermodynamics alone, how it is possible that
the effective viscosity coefficient of an isotropic colloidal system depends on
both the shear rate and the frequency.

I. INTRODUCTION

Much is known about the hydrodynamic description of colloidal systems. This is de-
scribed in a number of well written books on the subject [1,2,3]. In these books a multitude
of details about the interesting behavior of suspended asymmetric colloidal particles in
shear flow is treated. What is not being done is to treat these systems in the context of
nonequilibrium thermodynamics. That such a treatment is possible becomes clear reading
the monograph by De Gennes [4,5] on The Physics of Liquid Crystals. Rather than going
into detail regarding the motion of individual particles he discusses, both the equilibrium
and the nonequilibrium properties of these materials, using thermodynamics. In this paper
we will apply nonequilibrium thermodynamics to these colloidal systems. As it is not our
intention to duplicate all the well described knowledge about the collective behavior of these
systems, we will focus on one aspect which has remained puzzling from the viewpoint of
nonequilibrium thermodynamics.

It is well-known that the viscosity in these systems depends on the shear rate. In view
of the fact that the shear rate is not a thermodynamic state variable, like, for instance, the
temperature, classical nonequilibrium thermodynamics, as explained in the classic mono-
graph by de Groot and Mazur [6], does not allow such a dependence. Books on colloidal
hydrodynamics explain this dependence in terms of the behavior of asymmetric suspended
particles in shear flow. The question we pose ourselves in this paper is: explain this de-
pendence using nonequilibrium thermodynamics alone. Interestingly enough Prigogine and
Mazur [7] already mentioned this problem as one of the three possible examples of their
method of internal variables. The orientation of the suspended particles was suggested as
such an internal variable. In de Groot and Mazur's book [6] the other two examples are
treated in detail but this one was not pursued. It had to wait for a better understanding

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of these systems. In this paper we will show that it is now possible to answer this question for a suspension of asymmetric colloidal particles. In addition to answering a question of principle, the treatment is simpler and more direct than the current explanations. It is also not restricted to dilute suspensions.

In the second section we give the Gibbs relation for an isotropic system with asymmetric colloidal particles. The particles are assumed to have a symmetry axis. A new term appears which gives the entropy change due to a change in a tensorial order parameter $\mathbf{Q}$. This order parameter characterizes the alignment of the particles [4,5]. This is precisely the new internal variable Prigogine and Mazur [7] needed. In the third section the resulting entropy production is presented. This leads to linear laws in which the viscous pressure tensor and the time rate of change of the order parameter are expressed in their conjugate thermodynamic forces. In the fourth section these laws are solved for the special case of stationary shear flow. An expression is found for the viscous pressure in terms of the shear gradient. Their ratio defines an effective viscosity. This effective viscosity is found to be a function of the shear. Crucial to obtain this result is the fact that the Onsager coefficients in general depend on the order parameter $\mathbf{Q}$ which is a state variable. This answers the principle question. We proceed in chapter five with a analysis of time dependent shear flow. It is found that this results in a frequency dependent effective shear viscosity. In the last section we derive a simple expression for the dependence of one of the Onsager coefficients on the order parameter to make this point clear beyond doubt.

II. THE GIBBS RELATION

In an isotropic suspension of particles, which are cylindrically symmetric, a tensorial order parameter $\mathbf{Q}$ appears as a new thermodynamic variables [4,5]. $\mathbf{Q}$ is a traceless symmetric tensor, which is defined as the ensemble average of $(\mathbf{aa} - \mathbf{1}/3)$, where $\mathbf{a}$ is a unit vector along the symmetry axis of one of the particles and $\mathbf{1}$ is the unit tensor. In an isotropic phase $\mathbf{Q}$ is, in the absence of any directing field, zero. In, for instance, a magnetic field $\mathbf{Q}$ is nonzero. Changes of $\mathbf{Q}$ lead to changes of the entropy. It is therefore important to take the order parameter along in the description of the system. The total differential of the entropy is given by the following Gibbs relation

$$T ds_v = du_v - \mu d\rho - \mu_s d\rho_s - \mathbf{w} : d\mathbf{Q} \tag{1}$$

Here T is the temperature, $s_v = \rho s$ the entropy density, $u_v = \rho u$ the internal energy density, μ the chemical potential of the solvent, ρ the solvent particle number density, μ_s the chemical potential of the suspended particles and ρ_s the suspended particle number density. The densities with a subscript v, in addition to ρ and ρ_s, are per unit of volume. $\mathbf{w}$ is the variable conjugate to $\mathbf{Q}$ and is given by

$$\mathbf{w} = -T \left(\frac{\partial s_v}{\partial \mathbf{Q}} \right)_{u_v, \rho, \rho_s} \tag{2}$$

Alternatively one may use the relation to the free energy f_v

$$\mathbf{w} = \left(\frac{\partial f_v}{\partial \mathbf{Q}} \right)_{T, \rho, \rho_s} \tag{3}$$

Furthermore : between two matrices signifies a double contraction. De Gennes [4 (page 48),5] writes as explicit expression for the free energy density

$$f_v\left(T,\rho,\rho_s,\mathbf{Q}\right) = f_v^0\left(T,\rho,\rho_s\right) + \frac{1}{2}A\left(T,\rho,\rho_s\right)tr\left(\mathbf{Q}.\mathbf{Q}\right) + \frac{1}{3}B\left(T,\rho,\rho_s\right)tr\left(\mathbf{Q}.\mathbf{Q}.\mathbf{Q}\right) + \bigcirc\left(\mathbf{Q}^4\right)$$

(4)

where $\bigcirc$ is the order symbol. Here tr signifies the trace of a matrix. Note that $tr\left(\mathbf{Q}.\mathbf{Q}\right) = \mathbf{Q}:\mathbf{Q}$. The resulting traceless symmetric conjugate variable is

$$\mathbf{w} = A\left(T,\rho,\rho_s\right)\mathbf{Q} + B\left(T,\rho,\rho_s\right)\overline{\overset{\circ}{\mathbf{Q}.\mathbf{Q}}} + \bigcirc\left(\mathbf{Q}^3\right)$$

(5)

where $\overline{\overset{\circ}{\mathbf{Q}.\mathbf{Q}}}$ is the traceless symmetric part of $\mathbf{Q}.\mathbf{Q}$. This relation may be inverted to give the order parameter in terms of its conjugate variable

$$\mathbf{Q} = A^{-1}\left(T,\rho,\rho_s\right)\mathbf{w} - A^{-3}\left(T,\rho,\rho_s\right)B\left(T,\rho,\rho_s\right)\overline{\overset{\circ}{\mathbf{w}.\mathbf{w}}} + \bigcirc\left(\mathbf{w}^3\right)$$

(6)

The typical size of A is of the order of $k_B T \rho_s$ where k_B is Boltzmann's constant.

III. THE ENTROPY PRODUCTION

Without the $\mathbf{Q}$ term the Gibbs relation is equivalent to the one used in de Groot and Mazur [6]. Note that they use densities per unit of mass while we use densities per unit of volume like de Gennes [4,5] is doing. The calculation of the entropy production, using the balance equations, is essentially identical to the one they give. The only difference is the appearance of a term due to the order parameter $\mathbf{Q}$. In order to describe the contributions of the order parameter to the dynamical behavior of the system we may restrict ourselves, using the Curie principle, to contributions of force-flux pairs which are symmetric traceless tensors. The rate of entropy production density, as a function of position $\mathbf{r}$ and time t, due to these contributions becomes

$$T\sigma_{tens}\left(\mathbf{r},t\right) = -\overline{\overset{\circ}{\mathbf{\Pi}}\left(\mathbf{r},t\right)}:\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)} - \mathbf{w}\left(\mathbf{r},t\right):\frac{d\mathbf{Q}\left(\mathbf{r},t\right)}{dt}$$

(7)

here $\overline{\overset{\circ}{\mathbf{\Pi}}}$ is the symmetric traceless part of the viscous pressure tensor and $\overline{\overset{\circ}{grad\mathbf{v}}}$ the symmetric traceless part of the velocity gradient.

The resulting linear laws are

$$\overline{\overset{\circ}{\mathbf{\Pi}}\left(\mathbf{r},t\right)} = -2\eta\,\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)} - \ell\mathbf{w}\left(\mathbf{r},t\right)$$
$$\frac{d\mathbf{Q}\left(\mathbf{r},\mathbf{t}\right)}{dt} = \ell\,\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)} - \ell_Q\mathbf{w}\left(\mathbf{r},\mathbf{t}\right)$$

(8)

Here we used that, $\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)}$ is odd and $\mathbf{w}\left(\mathbf{r},\mathbf{t}\right)$ even for time reversal,so that the matrix of Onsager coefficients is antisymmetric. The Onsager coefficients are in general functions of the thermodynamic state variables, so that we have

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$$\eta\left(T,\rho,\rho_s,\mathbf{Q}\right), \qquad \ell\left(T,\rho,\rho_s,\mathbf{Q}\right) \quad \text{and} \quad \ell_Q\left(T,\rho,\rho_s,\mathbf{Q}\right) \tag{9}$$

In line with the assumption of linearity, they are not allowed to be functions of $\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)}$ and $d\mathbf{Q}\left(\mathbf{r},\mathbf{t}\right)/dt$. The diagonal coefficient η is the viscosity and the diagonal coefficient ℓ_Q is a typical rotational mobility of the suspended particles divided by ρ_s. The cross coefficient ℓ is dimensionless and is expected to be a positive constant of the order unity.

IV. STATIONARY ELONGATIONAL FLOW

The above equations may easily be solved for stationary elongational flow

$$\mathbf{v}\left(\mathbf{r},t\right) = \frac{1}{2}\,\dot{\gamma}\,\left(y,x,0\right) \tag{10}$$

The resulting velocity gradient is

$$\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)} = grad\mathbf{v}\left(\mathbf{r},t\right) = \frac{1}{2}\,\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{11}$$

Using the second linear law, eq.(8b), results in

$$\mathbf{w}\left(\mathbf{r},\mathbf{t}\right) = \frac{\ell}{\ell_Q}\,\overline{\overset{\circ}{grad\mathbf{v}}\left(\mathbf{r},t\right)} = \frac{\ell}{2\ell_Q}\,\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{12}$$

Substitution in eq.(6) gives

$$\mathbf{Q} = \frac{\ell}{2A\ell_Q}\,\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \bigcirc\left(\dot{\gamma}^2\right) \tag{13}$$

The first linear law, eq.(8a), then yields

$$\overline{\overset{\circ}{\mathbf{\Pi}}\left(\mathbf{r},t\right)} = -\left(\eta + \frac{\ell^2}{2\ell_Q}\right)\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \equiv -\eta_{eff}\,\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{14}$$

Writing the dependence on the thermodynamic state variables explicitly, the effective viscosity becomes

$$\eta_{eff}\left(T,\rho,\rho_s,\mathbf{Q}\right) = \eta\left(T,\rho,\rho_s,\mathbf{Q}\right) + \frac{\ell^2\left(T,\rho,\rho_s,\mathbf{Q}\right)}{2\ell_Q\left(T,\rho,\rho_s,\mathbf{Q}\right)} \tag{15}$$

In view of the above relation of the order parameter with the rate of elongation, one may write this relation as

$$\eta_{eff}\left(T,\rho,\rho_s,\dot{\gamma}\right) = \eta\left(T,\rho,\rho_s,\dot{\gamma}\right) + \frac{\ell^2\left(T,\rho,\rho_s,\dot{\gamma}\right)}{2\ell_Q\left(T,\rho,\rho_s,\dot{\gamma}\right)} \tag{16}$$

The effective viscosity depends therefore on the rate of elongation.

V. OSCILLATORY ELONGATIONAL FLOW

The above equations may also easily be solved in the case of oscillatory elongational flow. In that case the velocity field, its symmetric traceless gradient, the order parameter and its conjugate variable all become proportional to $\exp(-i\omega t)$. We now neglect the nonlinear terms in eq.(5) and the $\mathbf{Q}$ dependence of the transport coefficients in order to avoid the appearance of higher order harmonics. Though this is an interesting phenomenon, it is not our present concern. In the second linear law we must now replace $d\mathbf{Q}(\mathbf{r},\mathbf{t})/dt$ by $-i\omega\mathbf{Q}(\mathbf{r},\mathbf{t})$. In the solution this implies that

$$\mathbf{Q} = A^{-1}\mathbf{w} = \frac{\ell}{A\ell_Q - i\omega}\overline{grad\mathbf{v}} \tag{17}$$

The resulting complex frequency dependent effective viscosity then becomes

$$\eta_{eff}(T,\rho,\rho_s,\omega) = \eta(T,\rho,\rho_s) + \frac{\ell^2(T,\rho,\rho_s)}{2\ell_Q(T,\rho,\rho_s)(1 - i\omega\tau(T,\rho,\rho_s))} \tag{18}$$

with a relaxation time

$$\tau(T,\rho,\rho_s) = \frac{1}{A(T,\rho,\rho_s)\ell_Q(T,\rho,\rho_s)} \tag{19}$$

This relaxation time is the reorientation time of the suspended particles due to rotational diffusion, and is therefore of the order of the rotational diffusion coefficient. It follows that $\omega\tau$ is the relevant Péclet number for rotational diffusion in an oscillating velocity field. For low frequencies the effective viscosity is enhanced by the coupling to the order parameter

$$\eta_{eff}(T,\rho,\rho_s,\omega = 0) = \eta(T,\rho,\rho_s) + \frac{\ell^2(T,\rho,\rho_s)}{2\ell_Q(T,\rho,\rho_s)} \tag{20}$$

This is the same result as found above, eq.(15), for the stationary case if one neglects the dependence of the coefficient on the order parameter. For high frequencies one finds

$$\eta_{eff}(T,\rho,\rho_s,\omega = \infty) = \eta(T,\rho,\rho_s) \tag{21}$$

Writing the complex viscosity as the sum of a real and imaginary part, $\eta_{eff} = \eta'_{eff} + i\eta''_{eff}$, one has

$$\eta'_{eff}(T,\rho,\rho_s,\omega) = \eta(T,\rho,\rho_s) + \frac{\ell^2(T,\rho,\rho_s)}{2\ell_Q(T,\rho,\rho_s)(1 + \omega^2\tau^2(T,\rho,\rho_s))} \tag{22}$$

and

$$\eta''_{eff}(T,\rho,\rho_s,\omega) = \frac{\omega\ell^2(T,\rho,\rho_s)}{2\ell_Q(T,\rho,\rho_s)(1 + \omega^2\tau^2(T,\rho,\rho_s))} \tag{23}$$

This last expression gives the elastic contribution to the complex viscosity.

VI. THE ONSAGER COEFFICIENTS

Nonequilibrium thermodynamics does not derive expressions for the Onsager coefficients. Like the thermodynamic derivatives of the entropy as for instance $A(T, \rho, \rho_s)$, they have to be either measured or calculated from a description in terms of the motion of the separate particles. Above we have given estimates of the typical order of magnitude of the various coefficients on the basis of the physical meaning of the coefficients and dimensional arguments.

As the shear dependence of the effective viscosity is the property we set out to find, we will pursue this element a bit further. One may write

$$\eta = \eta_0 \left(1 + [\eta] \phi\right) \tag{24}$$

where $\phi = V\rho_s$, with V the volume of the monodisperse suspended particles. $[\eta]$ is the so-called intrinsic viscosity. Each suspended particle contributes to the viscous dissipation. For low densities the intrinsic viscosity is independent of their concentration. Einstein [8] found that the intrinsic viscosity for spheres was equal to 2.5. For rods the contribution depends on the orientation $\mathbf{a}$ of the rod. In order to get the intrinsic viscosity one must then first calculate the contribution of a rod to the viscous pressure tensor as a function of its orientation and then average over the orientations [2].

The distribution over orientations may be calculated using the rotational diffusion equation for this distribution. For the stationary state distribution corresponding to a given order parameter $\mathbf{Q}$ one has

$$f(\mathbf{a}) = \frac{15}{8\pi} \left(\mathbf{aa} - \frac{\mathbf{1}}{3}\right) : \mathbf{Q} + \frac{1}{4\pi} \tag{25}$$

For spheroids, which are useful as a model system, the solution of the velocity field has been given by Jeffery [9]. In the monograph by van de Ven [2] the resulting contribution to the pressure tensor is given. In the appendix we average those expressions over the above orientation distribution. This results in

$$
\begin{aligned}
[\eta] = \frac{2}{15} \left(r_e^2 - 1\right) &\left[\frac{5\ell}{4 \left(2r_e^2 - (1 - 2r_e^2) A_e\right)} \frac{\dot{\gamma}}{A\ell_Q} \right. \\
&\left. + \frac{26r_e^2 - 24r_e^2 A_e - 15A_e}{(2r_e^2 - 3A_e)(2r_e^2 - (2r_e^2 + 1) A_e)} + \frac{6}{(r_e^2 + 1)(3A_e - 2)} \right]
\end{aligned} \tag{26}
$$

Here the aspect ratio $r_e = a/b$ is the ratio of the diameter a along the symmetry axis and the diameter b normal to the symmetry axis. Furthermore

$$A_e = \frac{r_e^2}{r_e^2 - 1} - \frac{r_e \operatorname{arccosh} r_e}{(r_e^2 - 1)^{3/2}} \qquad \text{for } r_e > 1$$

$$A_e = \frac{r_e \arccos r_e}{(1 - r_e^2)^{3/2}} - \frac{r_e^2}{1 - r_e^2} \qquad \text{for } r_e < 1 \tag{27}$$

Note that $\dot{\gamma}/A\ell_Q$ is the rotational Péclet number so that eq.(26) is an expansion in the Péclet number. In the limit of a sphere, $r_e \to 1$, one may verify that the expression reduces to 2.5. In that case the shear dependence of the effective viscosity disappears. Prolate spheroids, $r_e > 1$, are shear thickening and oblate spheroids, $r_e < 1$, are shear thinning for small Péclet numbers in elongational flow [10].

VII. DISCUSSION AND CONCLUSIONS

The main objective was to show that a straightforward application of nonequilibrium thermodynamics leads to a shear dependent viscosity. We were able to derive a general nonlinear expression for this dependence. The important reason for this is the coupling to the orientation of the suspended colloidal particles. This orientation is described by a tensorial order parameter $\mathbf{Q}$ as thermodynamic state variable. The fact that the Onsager coefficients depend on this state variable then results in a shear dependent viscosity. Of course the critical reader could have doubted such a dependance of the Onsager coefficients on $\mathbf{Q}$. In order to defend us against this critique, we derive an explicit formula for small Péclet numbers, $\dot{\gamma}/A\ell_Q$. This gives a linear relation for this dependence. For larger Péclet numbers the nonlinear relation between $\mathbf{Q}$ and $\mathbf{w}$ must be taken into account. This will lead to more realistic and interesting predictions. One interesting aspect is that the powers of $\mathbf{Q}$ lead to shear field with a different "direction". As the principle question, *why the viscosity depends on the shear*, has been answered, we will not here pursue these points.

The frequency dependence is due to a single exponential decay of the order parameter. For low frequencies the viscosity is enhanced by the coupling to the orientation of the colloidal particles. For higher frequencies the orientation lags behind. This leads to thinning of the fluid and a reversible elastic response. One can extend the analysis, within the general frame of nonequilibrium thermodynamics, by introducing the whole angular distribution of the particles as an internal thermodynamic variable [6]. The details for such an analysis have recently been worked out by Mazur [11]. This results in a whole spectrum of relaxation times and consequently gives a more complex frequency dependence in the transition from low frequency to high frequency behavior.

In our analysis we do not need to analyse the orientational distribution function in any detail. The knowledge of the order parameter is enough. This makes our analysis much simpler that the usual procedure, where the rotational diffusion equation for this distribution function is solved numerically. As we said above [11], the orientational distribution function can be introduced as an internal thermodynamic variable. In addition to a richer frequency dependence this will also lead to a more complex shear dependence.

The low frequency and the low shear behavior of the viscosity has a very similar non-analytic dependance on these parameters [12]. This is a general phenomenon which is not specifically due to the asymmetry, or for that matter the presence, of the suspended particles. It falls outside the scope of the present article.

In the field of socalled extended irreversible thermodynamics [13], one assumes that fluxes, fluxes of fluxes, etc., are also thermodynamic state variables. This assumption distinguishes it from classical irreversible thermodynamics, where this is not considered to be a proper assumption. The viscous pressure is such a flux and is, according to extended irreversible thermodynamics, a state variable. On the basis of this assumption the viscosity can be a function of the viscous pressure. As a result, the viscosity then becomes a function of the shear. The assumption, so to say, defines the problem away. We will not try to invalidate their assumption. We only want to stress that the present paper shows that such an assumption is not needed to obtain a shear dependent viscosity. As such their assumption seems to be one to many.

VIII. APPENDIX

We use the results of Jeffery [9] as presented in van de Ven's monograph [2], see in particular pages 229-231. The shear field he uses is $v_1 = v_2 = 0$ and $v_3 = Gx_2$. In our notation $x = x_2, y = x_3, z = x_1, \phi = c$ and $\dot{\gamma} = G$. The symmetric traceless part of this simple shear field is identical to the one we used above. In view of the linearity of the problem we may therefore use the symmetric traceless part of the contribution to the viscous pressure tensor van de Ven uses:

$$\mathbf{\Pi} = \mathbf{\Pi}_0 + \frac{8\pi\eta_0}{V}\phi \langle\mathbf{M}\rangle \tag{28}$$

where $V = 4\pi b^3 r_e/3$ is the volume of the particle. $\mathbf{\Pi}_0 = -2\eta_0 grad\mathbf{v}(\mathbf{r}, t)$ is the viscous pressure one would have in the absense of the suspended particles. He gives the tensor $\mathbf{M}$ as $\mathbf{M}'$ in eq.(3.280) in a coordinate frame attached to the particle. Using the distribution given above, eq.(25), we have

$$\langle\mathbf{M}\rangle = \frac{15}{8\pi}\left[\int \mathbf{M}(\mathbf{a})\left(\mathbf{aa} - \frac{\mathbf{1}}{3}\right)d\Omega\right] : \mathbf{Q} + \frac{1}{4\pi}\int \mathbf{M}(\mathbf{a})\,d\Omega \tag{29}$$

where $d\Omega = \sin\theta d\theta d\phi$ with $0 < \theta < \pi$ and $0 < \phi < 2\pi$. The integral between square brackets gives a constant times the four index symmetric traceless unit tensor $\mathbf{\Delta}$. The matrix elements of this tensor are given by

$$\Delta_{ijkl} = \frac{1}{2}\delta_{ik}\delta_{jl} + \frac{1}{2}\delta_{il}\delta_{jk} - \frac{1}{3}\delta_{ij}\delta_{kl} \tag{30}$$

The constant can be calculated by taking $i = l$, $j = k$ and summing over i and j. This results in

$$\langle\mathbf{M}\rangle = \frac{3}{16\pi}\left[\int \mathbf{M}(\mathbf{a}) : \left(\mathbf{aa} - \frac{\mathbf{1}}{3}\right)d\Omega\right]\mathbf{Q} + \frac{1}{4\pi}\int \mathbf{M}(\mathbf{a})\,d\Omega \tag{31}$$

The contraction of two matrices is independent of the reference frame and we may therefore use the reference frame attached to the particle. In this reference frame $(\mathbf{aa} - \mathbf{1}/3) = (2/3)\mathbf{e}_1\mathbf{e}_1 - (1/3)\mathbf{e}_2\mathbf{e}_2 - (1/3)\mathbf{e}_3\mathbf{e}_3$ in terms of the unit vectors in this frame. This gives

$$\langle\mathbf{M}\rangle = \frac{1}{16\pi}\left[\int (2M'_{11} - M'_{22}(\theta, \phi) - M'_{33}(\theta, \phi))\,d\Omega\right]\mathbf{Q} + \frac{1}{4\pi}\int \mathbf{M}(\theta, \phi)\,d\Omega \tag{32}$$

Using eq.(3.280) we see that M'_{22} and M'_{33} integrate to zero while M'_{11} is independent of direction. In the second integral we can use eqs.(3.282)-(3.284) to obtain the only nonzero contribution. The result is

$$\langle \mathbf{M} \rangle = \frac{1}{2} M'_{11} \mathbf{Q} + \frac{b^3 r_e}{6} \left(\frac{4}{15} C_1 + \frac{1}{3} C_2 + \frac{2}{3} C_3 \right) \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{33}$$

Substitution of $\mathbf{Q}$ then yields

$$\langle \mathbf{M} \rangle = \left[\frac{\ell}{4 A \ell_Q} M'_{11} + \frac{b^3 r_e}{6} \left(\frac{4}{15} C_1 + \frac{1}{3} C_2 + \frac{2}{3} C_3 \right) \right] \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{34}$$

Substitution into eq.(28) and comparing with eq.(24) gives for the intrinsic viscosity

$$[\eta] = \left[\frac{\ell}{A \ell_Q} \frac{3 M'_{11}}{2 b^3 r_e} + \frac{4}{15} C_1 + \frac{1}{3} C_2 + \frac{2}{3} C_3 \right] \tag{35}$$

Substitution of eqs.(3.280) and (3.284) finally gives eq.(26).

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